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MULTIPLE FLOW REGIMES IN THE EXTRUSION OF NITROCELLULOSE BASED PROPELLANT DOUGHS

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MULTIPLE FLOW REGIMES IN THE EXTRUSION OF NITROCELLULOSE BASED PROPELLANT DOUGHS

R.C. Warren and A.T. Starks

ABSTRACT

Flow curves of triple, double, and single base propellant doughs were determined with an extrusion rheometer. In most cases the curves displayed an inflection which was associated with a critical stress in the dough. The critical stress caused the flow to separate into a high stress layer near the boundary of the flow, and a low stress region in the centre of the flow. The critical stress was also associated with flow instabilities. An explanation of the flow behaviour based on the Doi-Edwards theory is presented. Keywords: Australia, Rheology, viscosity index (GC/AW)

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1. INTRODUCTION

A recent study of the rheology of triple base propellant doughs revealed the presence of an inflection in the flow curves associated with a critical stress(ref.1). At low shear rates the flow curve had a slope of about 0.5, in common with many other polymeric materials. At the critical stress the dough underwent an apparent slip, and a second flow regime was established where the extrusion stress increased very slowly with increasing shear rate. The slope of the flow curve was about 0.2. It was shown that the apparent slip was not due to lack of adhesion between the dough and the die walls, and it was suggested that the apparent slip was due to fibrils sliding over each other, lubricated by the water from the processing solvent. However, similar behaviour has been subsequently observed in propellant doughs which contained a maximum of 0.3% water, and therefore the critical stress must be caused by some other property of the propellant dough. This critical stress is different from the yield stress observed in many propellant doughs(ref.2), because the critical stress occurs at moderate shear rates, whereas the yield stress occurs at vanishingly small shear rates.

This paper has two aims: firstly to present experimental observations of the critical stresses and multiple flow regimes in a range of single, double and triple base propellant doughs, and secondly to provide an explanation of the critical stress and multiple flow regime behaviour based on the Doi-Edwards theory of molecular behaviour. The application of the Doi-Edwards theory to propellant dough rheology, reported for the first time here, has resulted in a breakthrough in the understanding of the flow problems in propellant manufacture, pointing the way to several methods of improving propellant processability.

2. EXPERIMENTAL

2.1 Materials

Single, double, and triple base propellant doughs were studied. The double base dough consisted of:-

Nitrocellulose(NC)(12.6%N)	53.8%
Nitroglycerine(NG)	22.5%
Stabilizer	2.9%
Cryolite	0.6%
Processing solvents	Added

The triple base doughs consisted of the double base matrix filled with picrite to levels of 15%, 30%, and 47.7% of the total weight without solvents. The latter composition was similar to the US triple base propellant designated M30. The compositions and processing solvent details are given in Table 1.

The single base propellant dough consisted of 99% NC(13.1%N) and 1% stabilizer, plus processing solvents.

2.2 Processing methods

The double base dough was made by mixing the paste and pre-mixed solvent for 10 min, adding the stablizer and cryolite and mixing for a further 2 hour. The mixing and extrusion temperatures were both 35°C. The triple base dough was produced in a similar manner, except that the picrite was added after the initial 10 min, mixed until bind-up, and then mixed for a further 2 hour.

Where necessary, drying back to extrusion consistency was achieved with a nitrogen purge before the 2 hour mixing step.

The single base doughs were made by mixing the ethanol-wet NC for 10 min at 20°C, then adding the acetone and dissolved stabilizer. Mixing was continued for 75 min at temperatures of either 20, 30, 40, 50, or 60°C, before mixing at 30°C for 15 min. The ethanol/acetone ratio was 1/1, and the solvent weight was 60% of NC weight.

TABLE 1. PROCESSING PROCEDURES FOR M30 TYPE DOUGHS

Code Number	Picrite (%)	Ethanol/Acetone Solvent		Mix/Extrusion Temperature (°C)
		Ratio	% on NC	
GP794	47.7	2/1	82.5	35/35
GP797	0	2/1	38	35/35
GP800	15	2/1	50	35/35
GP801	30	2/1	68.5	35/35
GP804	47.7	2/1	81.5	35/35
GP805	47.7	0.37/1	111*,**	30 to 60/34
GP807	47.7	0.37/1	111**	35/35
GP808	0	0.37/1	52**	35/35

* GP805 contained triacetin, and the mix cycle involved several temperature changes.

** GP805, GP807, and GP808 were oversolvated and dried back.

An unusual mix procedure was adopted for GP805 to model, using a batch mixer, a solvent process for use in a screw mix-extruder. In this process, the NC was added in the alcohol-wet state, and the NG was added dissolved in the solvent. Since neat NG was not available, Type 3 casting liquid (consisting of 80%NG and 19%TA with 1% stabilizer) was used. The alcohol wet NC, picrite, stabilizer and cryolite were added to the mixer and mixed for 20 min at 30°C. Half the acetone with the casting liquid was added and mixed for 15 min at 30°C. The remaining acetone/casting liquid was added and mixing continued at 60°C for 25 min. The lid of the mixer was opened and mixing continued for 75 min between 40 to 60°C. The lid was closed and final mixing was carried out at 30°C for 70 min.

GP805, GP807 and GP808 were oversolvated during incorporation and then dried back to extrusion consistency after dough-up. Unfortunately the final solvent levels were not recorded.

2.3 Rheological testing

Rheological testing was carried out in an extrusion rheometer consisting of a water jacketed barrel with an internal diameter of 32 mm and a length of

180 mm, and a ram driven at constant rates by an Instron machine. There was provision for various types of dies in water jacketed holders to be attached to the bottom of the barrel. Two die configurations were used in this work; capillary dies, and a slit die.

The capillary dies had diameters 0.91 mm, 3.27 mm, and 6 mm, and a length to diameter ratio of 10:1. The pressure required to extrude dough through the capillaries was measured by a transducer mounted in the barrel just above the die entrance. The capillary dies were mainly used for measuring die swell with a line scan camera.

The flow channel in the slit die was 0.98 mm thick, 10.0 mm wide and 28.3 mm long. A miniature pressure transducer was flush mounted in the wall of the slit along the centreline at a distance of 16.2 mm from the slit exit to measure pressure drop in the slit.

Shear stress and shear rate at the die walls were calculated from the standard formulae:-

For capillary dies

$$\sigma_a = \frac{P.D}{4\ L} \tag{1}$$

$$\dot{\gamma}_a = \frac{32Q}{\pi D^3} \tag{2}$$

where σ_a and $\dot{\gamma}_a$ are the apparent shear stress and shear rate respectively, P is the pressure drop along a die of diameter D and length L, and Q is the volume flow rate of dough. Corrections for entrance pressure loss were not made, so the shear stresses reported for capillary dies will be apparent and not true shear stresses.

Shear rates reported here, for both capillary and slit dies, are also apparent values. A procedure exists for calculating true shear rates, the Rabinowitsch procedure(ref 3), but it is not accurate when the slope of the flow curve is low, as is the case of the flow regimes where much of the interest of this work lies.

For slit dies

$$\sigma = \frac{P.h}{2\ L} \tag{3}$$

$$\dot{\gamma}_a = \frac{6Q}{wh^2} \tag{4}$$

where h and w are the slit thickness and width respectively, and P is the pressure measured by a transducer mounted a distance L from the end of the die. The shear stress calculated in this way is the true shear stress, as the entrance pressure loss is not involved.

3. RESULTS

3.1 Double and triple base propellants

3.1.1 Flow curves

Unless otherwise stated, all the flow curves are plots of log true shear stress vs log apparent shear rate, calculated from data obtained from the slit die.

The flow behaviour of the 47% picrite doughs GP794, GP804, GP805, and GP807 at 35°C is illustrated in figure 1. It can be seen that in all but one case the flow curves consisted of two regions, one of moderate slope at shear rates up to about 5 s^{-1} and a second of moderate slope at high shear rates. The two regions were separated by a plateau region of low slope, which was defined by the critical stress of about 75 MPa. GP807 showed decrease in shear stress with increasing shear rate at low shear rates, and this effect was reproducible.

The similarity of the flow curves for GP794, GP804 and GP805 was surprising in view of their differences in solvent strength, and hence in degree of gelatinization. The composition of GP805 also differed from the others in that it contained triacetin.

The flow curves for the same doughs at 50°C are given in figure 2. At this temperature there appear to be significant differences in the behaviours of the doughs. The critical stresses of doughs GP794 and GP804 have now dropped, while the values for GP805 and GP807 remain similar to the values at 35°C. The GP805 and GP807 doughs are much more highly gelatinized than the other doughs, but it is not clear if this could explain the effect of the temperature on critical stress.

The effect of picrite content on flow curves of poorly gelatinized doughs is illustrated in figures 3 to 5. Figure 3 gives the flow curves at 20°C. There is a general trend for the flow curves to drop to lower values with increasing picrite content, although it is not clear whether this is an inherent effect of the picrite, or whether it is due to differences in processing solvent level. There appeared to be a critical shear stress in the range 100 to 200 MPa in most of the curves.

Increasing the picrite level had a large effect on the flow curves at 35°C and 50°C. -At 35°C the double base matrix gave a flow curve with a high slope at low shear rates, until the critical stress was reached, where the curve showed a sharp break, see figure 4. For the other doughs the slope at low rates decreased on addition of picrite, and the change in slope at the critical stress became progressively less. The same trends were apparent at 50°C, see figure 5.

The value of the critical stress appeared to decrease with increasing picrite content.

The effect of changing the degree of gelatinization of the matrix is illustrated in figure 6. The poorly gelatinized dough was processed using a solvent with an ethanol/acetone ratio of 2/1 and a concentration of 38% by weight of NC, and the well gelatinized dough was processed using a solvent with an ethanol/acetone ratio of 0.37/1, but the solvent concentration in the dough was not known. The flow curves of the two doughs were similar above the critical stress, but the curve for the well gelatinized dough was significantly above the poorly gelatinized curve in the low stress regime.

The effect of temperature on the flow curves was similar in all cases, but it was most clearly shown for the unfilled matrix GP797, see figure 7. At 20°C the whole flow curve appeared to be above the critical stress. At 35°C the critical stress was reached at a shear rate of about 2 s^{-1}, and at 50°C the critical stress was reached at about 9 s^{-1}. The value of the critical stress appeared to decrease slightly with increasing temperature.

In figure 1 the well gelatinized, 47% picrite dough GP807 at 35°C showed a decrease in shear stress with increasing shear rates in the low shear rate region. To further investigate this apparently anomalous behaviour, a run was made at 65°C instead of 20°C. The flow curves for 35, 50 and 65°C are given in figure 8. It can be seen that the curve for 65°C had a region of positive slope at low rates, which was similar to the curves of other doughs at lower temperatures. Hence the unusual behaviour at 35°C may be due in part to the very high viscosity of this dough at low temperatures, which in turn may have been due to a low solvent level.

3.1.2 Pressure-time traces

The flow curves were determined by starting the flow at the lowest extrusion rate and allowing the pressure to reach a steady value, which was assumed to be the equilibrium pressure for that extrusion rate. Pressures for higher rates were obtained in a similar manner by stepping sequentially up the extrusion rate range. However, stepping up the extrusion rate to higher values often caused the pressure-time curve to overshoot and then drop back to an equilibrium level. The magnitude of the overshoot tended to increase with increasing shear rate, particularly in the flow regime above the critical stress. This type of transient overshoot behaviour is observed in many polymeric systems, but the timescale is usually shorter.

An anomalous type of transient behaviour was observed in doughs GP800, GP805, GP807 and GP808, at stresses just above the critical stress. A pressure time trace for GP808 in the 3.27 mm diameter capillary die is given in figure 9. The step increases in rate to 0.4 and 0.8 s^{-1} produced a normal increase in extrusion pressure. However, increasing the rate to 1.9 s^{-1} caused an overshoot which led to an oscillation in pressure. Dropping the rate and increasing it again produced the same result. Increasing the rate to 3.8 s^{-1} causes the pressure to undergo the peculiar behaviour shown in figure 9 before settling on an equilibrium value. It is believed that this behaviour is related to flow instabilities in propellant extrusion, and a possible explanation of this behaviour will be given in Chapter 4.

3.1.3 Demonstration of the absence of wall slip

To confirm the results obtained in the previous study on NQ doughs(ref.1), it was decided to test whether wall slip was a factor in the flow of the present doughs. Dough GP808 was chosen because there would be no extraneous effects from fillers. Extrusions were made through dies with diameters 2.34, 3.27 and 6 mm, each with a length/diameter ratio of 10. The resulting flow curves are given in figure 10. It can be seen that the flow curves superimpose very well, even above the critical stress, which would not be the case if the critical stress was due to wall slip. See reference 1 for further details of the method of determining whether wall slip occurs in propellant dough.

3.1.4 Die swell

Since the main thrust of this work was to investigate the flow curves of the propellant doughs, extrusion measurements were made with the slit die in order to give true shear stress directly from extrusion pressure. The use of capillary dies would have required measurements with multiple dies to calculate the entrance pressure loss corrections. This procedure would have smoothed out some of the interesting features of the flow curves, and may be one of the reasons why a critical stress was not seen in a previous study(ref.2). While it was not possible to measure die swell with the slit die, this was not a serious drawback for the poorly gelatinized doughs, as their die swell would have been quite small. In the cases where die swell of poorly gelatinized doughs extruded from capillary dies was measured, it rarely exceeded about 5%.

Previous experience indicated that the die swell of well gelatinized doughs would be large, and this was confirmed by measurements on the unfilled dough GP808. The die swell from the 3.27 mm die at 50°C is given in figure 11. The values at high rates are averages, as the cord suffered severe distortion from flow instability. There appears to be an abrupt increase in die swell starting at a shear rate of about 2 s^{-1}, which coincided with the rate at which the critical stress is reached; see figure 6.

3.1.5 Extrudate quality

The quality of surface finish of the filled extrudates varied between smooth and matt under various circumstances, but there was no evidence of large scale unstable flow or melt fracture. The filled doughs have lower elasticity and propensity to unstable flow because the presence of fillers dilutes the elastic matrix component. Hence cords of the unfilled doughs were examined to determine the effect of extrusion rate on surface quality because these doughs would be more sensitive to processing variations.

The well gelatinized dough GP808 was extruded through capillary dies of diameter 2.34, 3.27 and 6.0 mm at 50°C. The cords from the 2.34 mm diameter die were relatively smooth with only scattered fissures up to a rate of about 1 s^{-1}, and above that rate a flow instability similar to melt fracture progressively set in. The cords from the 3.27 mm diameter die were shiny at about 0.3 s^{-1}, and surface fissuring increased up to a rate of about 3 s^{-1}, where melt fracture set in. The 6 mm diameter cord had a surface with moderately deep fissures up to a rate of about 1 s^{-1}, and melt fracture set in at about 4 s^{-1}. In each case melt fracture set in when the stress reached or just exceeded the critical stress; see figure 6.

The poorly gelatinized dough GP797 was extruded through the 3.27 mm diameter capillary at 50°C. At the lowest shear rate the cord was very smooth, but the finish slowly deteriorated with increasing rate, with a maximum degree of mattness at about 2 s^{-1}. Above this rate the surface quality improved up to a rate of about 2000 s^{-1}, where melt fracture appeared to set in.

3.1.6 Layers in extrudates

Evidence of layered flow was observed on the ends of 8 mm diameter single perforate propellant grains cut from extruded cords of filled propellant doughs. This evidence took the form of dark bands about 0.5 to 1 mm thick near the outer surface and also around the perforations of grains of both triple base propellants and single base propellants. A photograph of a typical single perforated grain of GP801 is given in figure 12. The perforation in the centre of the grain has completely closed and is not visible. The dark ring in the centre is the high shear rate layer, and this is surrounded by the lighter low shear rate region. The shear rate on the outside of the grain was lower than the shear rate around the perforation, and so the layer on the outside of the grain is not as dark as the centre layer.

Thin slices cut axially from cords of the unfilled doughs were examined under a microscope with crossed polarisers. Cords extruded at moderate and high shear rates had a highly birefringent surface layer, but there was little or no evidence of a birefringent layer at low rates. The presence of birefringence indicated that the NC molecules were aligned relative to the surface. The layers in the poorly gelatinized cords appeared to be fairly uniform in thickness, but the layers in the well gelatinized cords showed large variations in thickness at different axial positions. The variations in layer thickness appeared to be associated with the gross distortions due to melt fracture. It proved to be impossible to obtain good photographs of the layers because of the presence of birefringent fibre fragments remaining in the cords.

3.2 Single base propellants

Flow curves were determined for single base propellant doughs manufactured under identical conditions, except that mix temperatures of 20, 30, 40, 50 and 60°C were used. Rheological measurements were made both at the mix temperature, and at 60°C, for each dough. The curves are given in figures 13 and 14. The effect of mix-extrusion temperature is illustrated in figure 13. It can be seen that as the temperature was increased the viscosity of the dough decreased, as expected, but the critical stress appeared to be unchanged. The similarity of the flow curves to those of the double and triple base doughs is readily apparent, and suggests that the critical stress is in some way associated with the NC. The flow curves of the doughs mixed at different temperatures, but measured at 60°C are given in figure 14. The curves overlap reasonably well, indicating that the mix temperature had little effect on extrusion behaviour at 60°C. However, there was a slight systematic increase in apparent viscosity as the temperature increased from 20°C to 60°C. This increase may have been caused by solvent loss during mixing at the higher temperatures.

4. DISCUSSION

4.1 Direct practical effects of multiple flow regimes

The results presented above immediately raise a number of questions of practical importance in propellant processing. The surface layers produced at high extrusion rate are much more highly oriented than the bulk material, and hence they should have different physical and mechanical properties. It is not obvious a priori whether the surface layer or the bulk would have the more desirable mechanical properties, and so it is not possible to say at this stage if the processing conditions should be altered to promote, or to diminish, the formation of an oriented layer. This question will be addressed in a separate study.

Deterrent diffusion is another area in which the existence of an oriented surface layer could be significant. The diffusion coefficient in the oriented region may be quite different from the diffusion coefficient in the unoriented bulk region, and this may alter the mechanism of deterent coating(for either better or worse). If the deterrent penetrated the surface layer more easily than the bulk, then the deterrent may accumulate principally in the surface layer. If the surface layer could be made very uniform, the variability of coating thickness would be reduced. However, if penetration of the surface was slower than for the bulk, it would add to the difficulty of uniformly coating propellant. The burning rate may also be different in the undeterred layer.

4.2 Molecular mechanism controlling multiple flow regimes

The flow behaviour of NC doughs can be explained, at least qualitatively, by recent developments in the theory of polymer flow based on the Doi-Edwards theory, which is described in a review by Pearson(ref.4). A detailed discussion of the Doi-Edwards theory is beyond the scope of this paper, but the main tenet relevant here is that there are a number of molecular relaxation process which occur over different time-scales, and the response of the polymer to deformation is given by the sum of these relaxations.

In order to better show the link between the results and theory, the important results will now be summarised. All of the nitrocellulose propellant doughs studied exhibited a critical shear stress. For flow at low shear rates the shear stress was below the critical shear stress, and only a single flow regime existed. At high shear rates the flow consisted of two regimes, one with stresses above, and the other with stresses below, the critical shear stress. The high stress flow produced a strongly oriented surface layer, and a low stress flow produced unoriented material in the centre of the flow. The thickness of the high stress layer may be expected to be proportional to the amount by which the stress at the wall exceeds the critical shear stress.

Some anomalous unstable transient flow was observed for shear stresses slightly above the critical shear stress. The well gelatinized unfilled dough also showed the onset of melt fracture when the stress reached the critical stress, and the die swell also increased rapidly above this stress.

The critical shear stress was largely independent of temperature, but it appeared to decrease with increasing picrite content and increasing solvent content.

The degree of gelatinization had little effect on the filled doughs, but it had some effect on the flow curves of the unfilled doughs. The poorly gelatinized doughs had very small die swell and only small surface irregularities, whereas the well gelatinized unfilled dough showed large die swell and was very distorted at high shear rates. The birefringent surface layers were also affected by the degree of gelatinization. Poorly gelatinized extrudates had relatively uniform surface layers, whereas the well gelatinized extrudates had layers of varying thickness, indicating that the interface between the high and low rate regimes was unstable in those extrudates.

All the behaviour listed above can be explained in a semi-quantitative way by the following theory developed by Lin(ref.5). and McLeish and Ball(ref.6). They used the Doi-Edwards theory to calculate the flow curve of an amorphous polymer with flexible entangled molecules. The molecular weight of the molecules, M, was assumed to be constant, and many times greater than the molecular weight between entanglements, Me. The calculated form of the flow curve is illustrated schematically in figure 15. It has a peak at low rates due to an entanglement relaxation process, a section of negative slope causing a trough at intermediate shear rates, and then a positive slope at high shear rates. Since the peak is due to entanglement relaxation, it is related to the plateau modulus of the polymer, Gn, which is given by

$$Gn = \frac{\rho RT}{Me} \tag{5}$$

where ρ is the density of the polymer, R is the gas constant, T is the absolute temperature. Gn can be determined from stress relaxation or dynamic mechanical measurements. The calculated peak height is approximately 0.15Gn.

The positive slope of the flow curve at high shear rates is associated with a molecular process having a short relaxation time. The separation between the entanglement relaxation and the short time process is determined by the ratio of the weight of molecule between entanglements, Me, and the total weight of the molecules, M. As illustrated schematically in figure 15, large values of M/Me give a trough which is very deep and has a long region of negative slope. On the other hand, for small values of M/Me the negative slope region may not exist. A negative slope first appears at a ratio of M/Me of about 10. The theory outlined above was derived for mono-disperse polymers. The effect of broadening the molecular weight distribution is to reduce the depth of the trough and reduce the length of the negative slope region.

The molecular characteristics of NC indicate that the Doi-Edwards theory should apply, in a semi-quantitative way, to the extrusion behaviour of NC propellant doughs. The weight and number average molecular weights of NC are about $Mw = 2.8 \times 10^5$ and $Mn = 4 \times 10^4$ respectively. In a compilation of lengths between entanglements of a wide range of polymers, Aharoni gave a value of Me for NC of 3.6 nm(ref.7). The length of one monomer ring is about 0.5 nm, so there are about 7 rings between entanglements, giving molecular weight between entanglements of about 1900. These molecular weight values give $Mw/Me \sim 150$, and $Mn/Me \sim 21$. The molecular weight ratios are greater than the required value of 10, and so the flow curve of NC should be sinuous. Substituting the appropriate values in equation (5) gives $Gn \sim 2 \times 10^6$ Pa, which is a value comparable to other polymers. Since the peak height is approximately 0.15Gn, its value in this case is 300 kPa.

There are a number of factors which qualify the above analysis. Theories of polymer deformation usually consider the molecule to be sufficiently flexible for Gaussian statistics to apply to the chain, and hence the theory of rubber elasticity can be used to calculate the restoring force on deformed molecules. However NC is a semi-rigid molecule, and it has yet to be determined if the formulae for flexible polymers can be used without some modification. Secondly, the value for Me quoted above would only apply to undiluted NC. The presence of solvents and plasticizers would decrease the NC molecule density, and hence increase Me. These factors may alter the quantitative relations derived above, but the qualitative description should still be valid.

The calculated peak height of about 300 kPa for the flow curve of pure NC would be reduced by the diluting effect of the solvents and plasticizers in propellant doughs. The observed value of the critical stress of about 100 kPa is a minimum value, as discussed later.

4.3 Stability of flow in the negative slope region

In controlled pressure flows of materials with flow curves like figure 15, increasing the pressure must eventually cause the flow to jump suddenly from one branch of the flow curve to the other; see figure 16. In controlled rate flows at rates in the negative slope region there can be no stable flow, and the flow must oscillate between the two branches of the curve in a hysteresis loop, as illustrated in figure 17. In practical rheometers the extrusion rate cannot be controlled precisely because of the compliance of the rheometer and the compressibility of the dough, which allow the shear rate and pressure to fluctuate under variations in load. Hence the magnitude of the hysteresis would depend on the properties of the individual rheometer and dough.

A clear case of oscillation in the negative slope region was found in the previous study of triple base NQ doughs(ref.1). The flow curve is illustrated in figure 18, where the lower limit of the stress oscillations is given by the dotted line. The flow rate would have fluctuated in a similar manner. It would be theoretically possible to investigate the trough using a rotary rheometer, but attempts to do so to date have failed because of the occurrence of flow instabilities, which may or may not be related to the extrusion instabilities.

Lin(ref.5) developed his theory in order to explain the "stick-slip melt fracture" observed in polyethylene and other polymers. He explained the spurt flow and fissuring in extrudates in terms of flow oscillations in the negative slope region. The fissuring which occurs in the poorly gelatinized unfilled dough near and above the critical stress may be related to a stick-slip oscillating flow.

4.4 Stability of flow in the high rate regime

Under conditions of steady flow in a long pipe, the shear stress is linearly proportional to the radius, as illustrated in figure 19. Hence, if the stress at the wall exceeds the critical shear stress, there will be a value of the radius corresponding to the critical shear stress which separates the high stress outer layer from the lower stress interior. The larger the amount by which the wall shear stress exceeds the critical shear stress, the thicker the high stress layer will be.

When the shear rate is high enough for flow to occur in the high rate regime, there are a multitude of possible flow patterns, because the critical stress can theoretically vary between the peak and the trough of the curve, and the interface can vary accordingly; see figure 20.

A stability analysis of flow occurring under these circumstances has been given by McLiesh(ref.8). The most energetically favourable flow occurs when the transition from low to high rate regime occurs at the lowest possible stress, Case (c) in figure 20. McLiesh calculated that in the flow of inelastic fluids the corresponding interface should be stable, and this was observed in the poorly gelatinized unfilled dough GP797. However, the situation is quite different in elastic doughs. The normal forces in elastic doughs cause a coupling across the interface which is subject to instability, and McLiesh postulated this as a cause of flow instability and melt fracture. In the well gelatinized unfilled dough, GP808, the flow instabilities appeared to be associated with the varying thickness of the surface layer, which gives an experimental indication of an unstable interface.

While the stable position of the interface in a long pipe is at the smallest radius, corresponding to the critical stress being at the bottom of the trough, the situation at the die entry may be different. McLeish(ref.8) calculated that in the entry region the interface would be closer to the wall than in the body of the die, and that some flow rearrangement would occur in the entry region. The establishment of a stable axial profile may take a finite time, which would explain the anomalous transient response occasionally observed when the extrusion rate was increased, see figure 9. In some cases a stable flow may not occur, giving rise to melt fracture.

Hence it appears to be quite possible that the flow instabilities which complicate propellant processing may be due to the multiple flow regimes associated with a sinuous flow curve.

5. CONCLUSIONS

Flow curves of single base, double and triple base propellant doughs have been measured with an extrusion rheometer. All the doughs were processed with acetone/ethanol solvents. The curves displayed an inflection which was associated with a critical shear stress. The critical shear stress was reached at low to moderate shear rates, and for stresses above the critical stress, the flow was divided into two regimes. A high shear stress layer occurred near the surface of the flow, and a low stress region occurred in the centre of the flow. At stresses near the critical stress the flow was occasionally unstable, and oscillations in pressure and flow rate occurred.

The value of the critical stress depended on picrite content, solvent content and, to a lesser degree, on temperature.

The thickness of the high stress layer was constant in the poorly gelatinized doughs, but the thickness of the layer in well gelatinized doughs appeared to fluctuate randomly. The fluctuating thickness was related to flow instabilities and gross melt fracture.

These observations can be explained by a molecular theory of flow based on the Doi-Edwards theory. The theory also explains the nature of some of the flow instabilities observed in NC propellant doughs.

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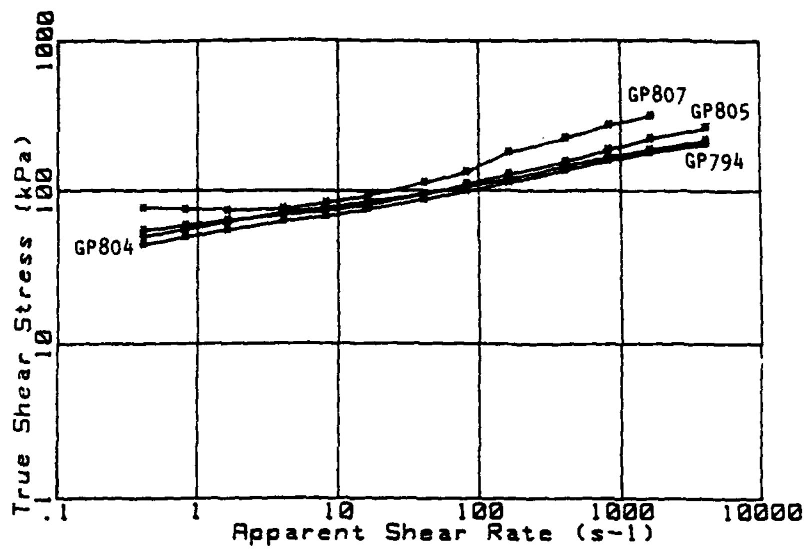

Figure 1. Flow curves of triple base doughs containing 47.7% picrite (temperature 35°C)

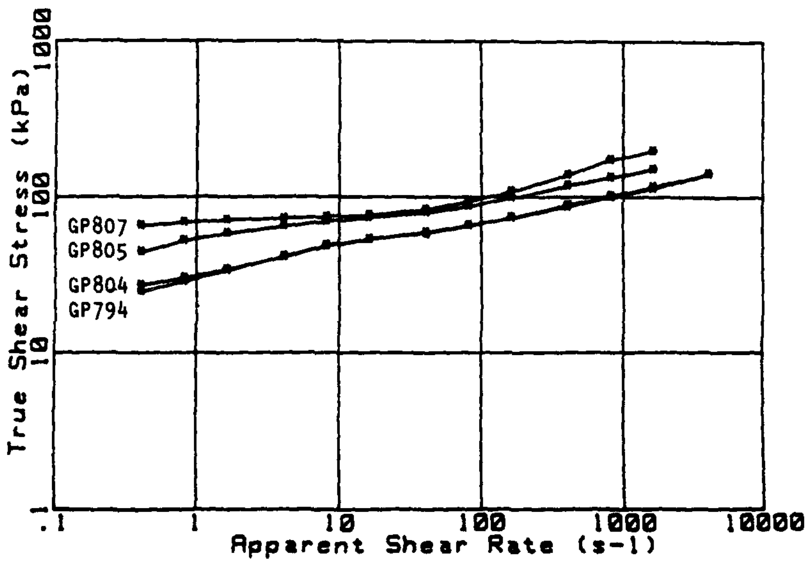

Figure 2. Flow curves of triple base doughs containing 47.7% picrite (temperature 50°C)

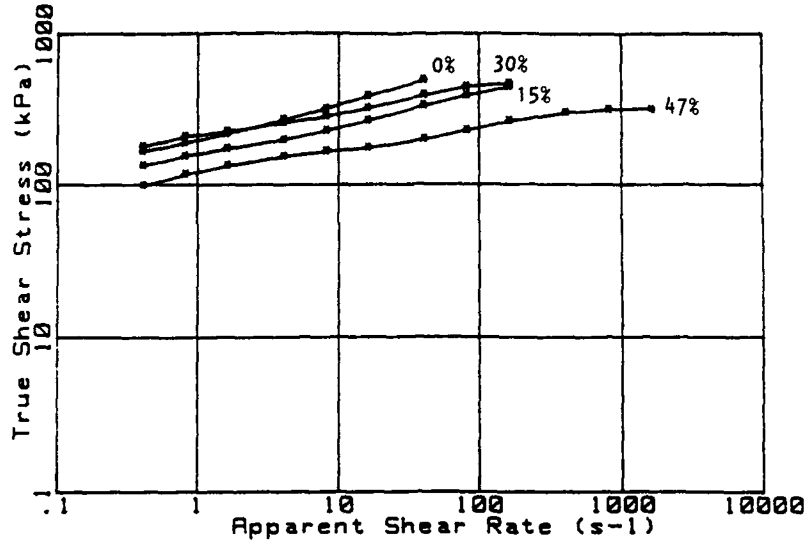

Figure 3. Flow curves of triple base doughs containing 15, 30 and 47.7% picrite, and the double base matrix (temperature 20°C)

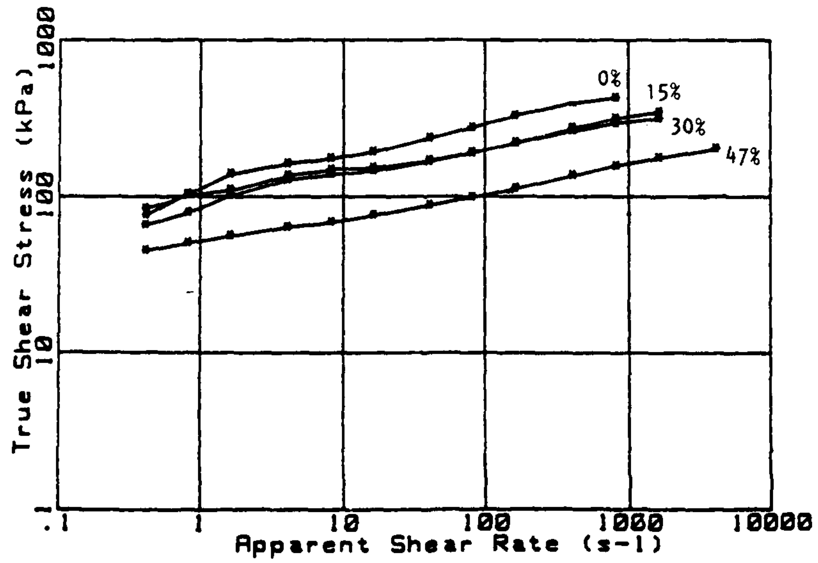

Figure 4. Flow curves of triple base doughs containing 15, 30 and 47.7% picrite, and the double base matrix (temperature 35°C)

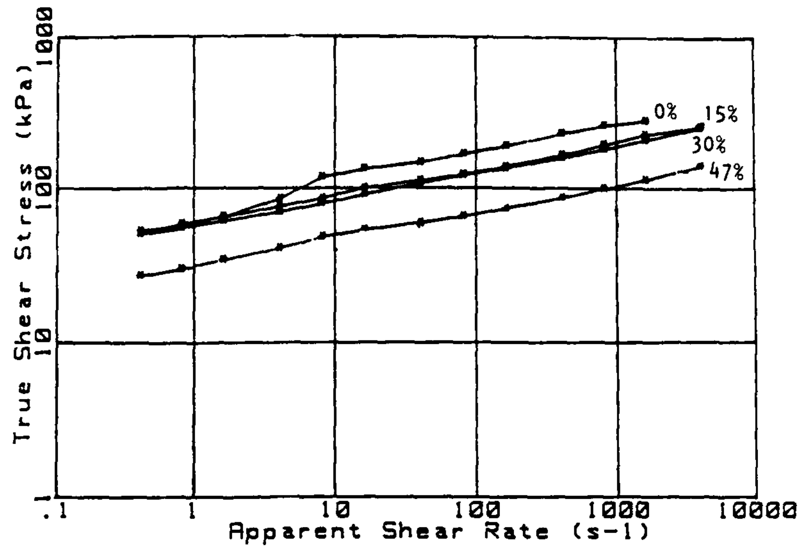

Figure 5. Flow curves of triple base doughs containing 15, 30 and 47.7%. picrite, and the double base matrix (temperature 50°C)

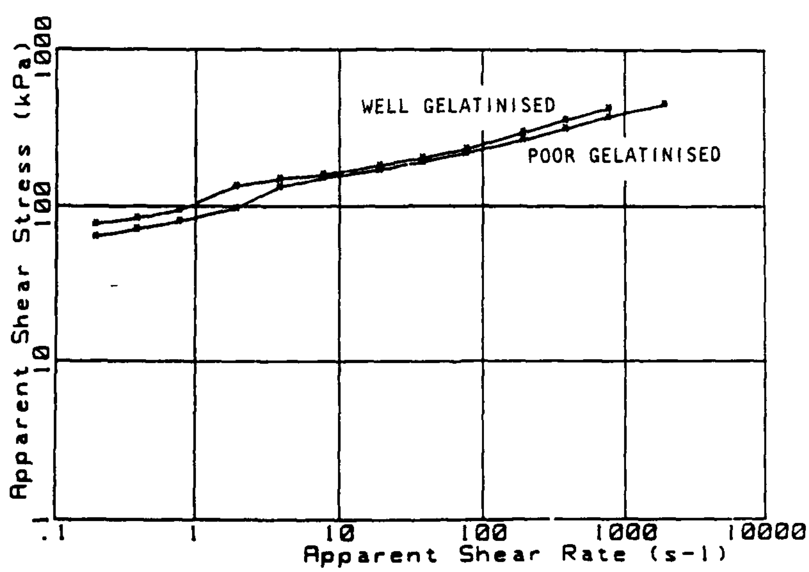

Figure 6. Flow curves of well and poorly gelatinized double base doughs (temperature 35°C)

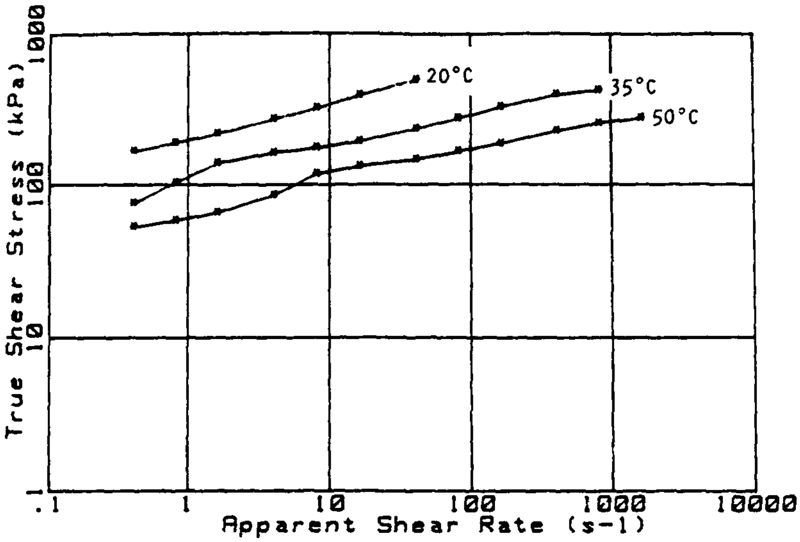

Figure 7. Effect of temperature on the flow curves of poorly gelatinized double base dough GP797

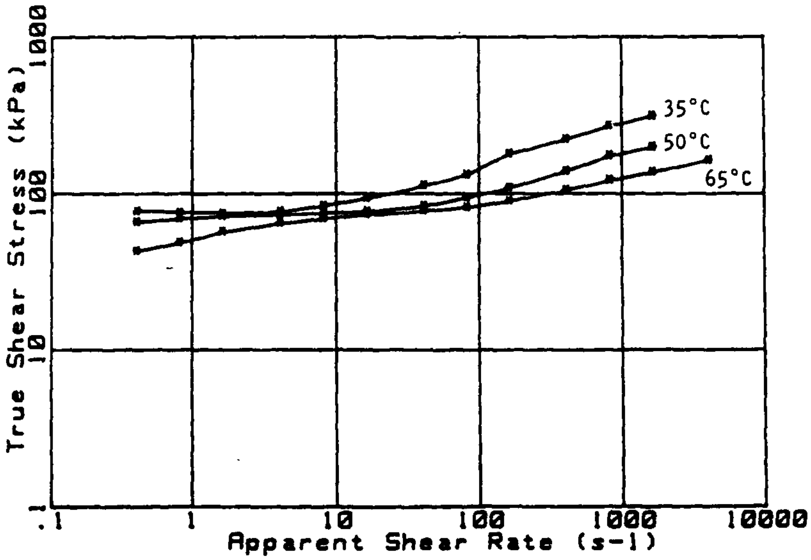

Figure 8. Effect of temperature on the flow curves of well gelatinized triple base dough GP807

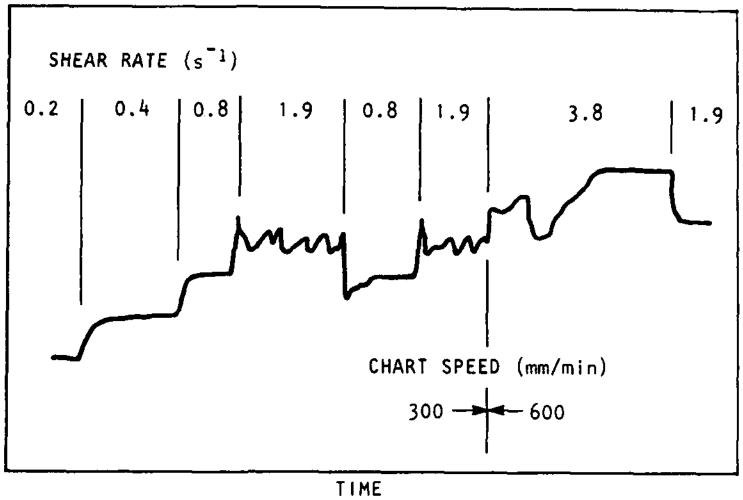

Figure 9. Anomalous pressure overshoot behaviour following increases of extrusion rate (GP808, 3.27 mm diameter die, 50°C)

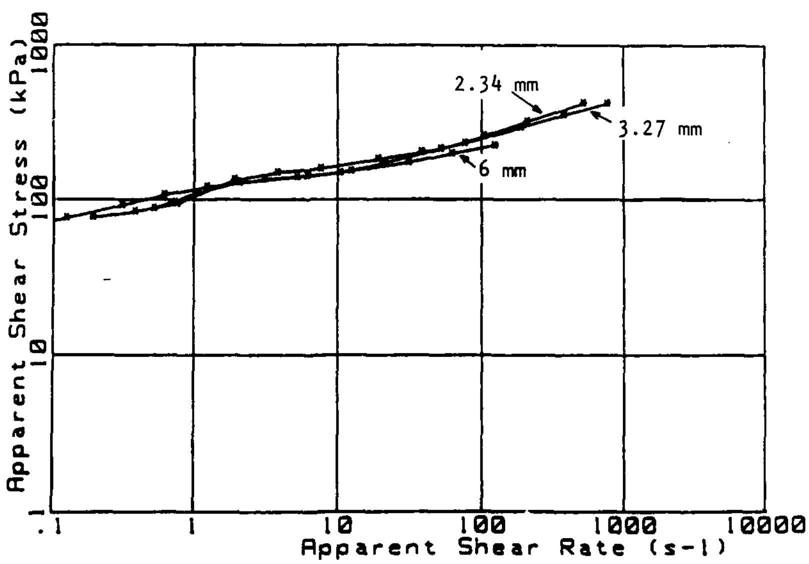

Figure 10. Flow curves of double base dough GP808 obtained from capillaries of various diameters

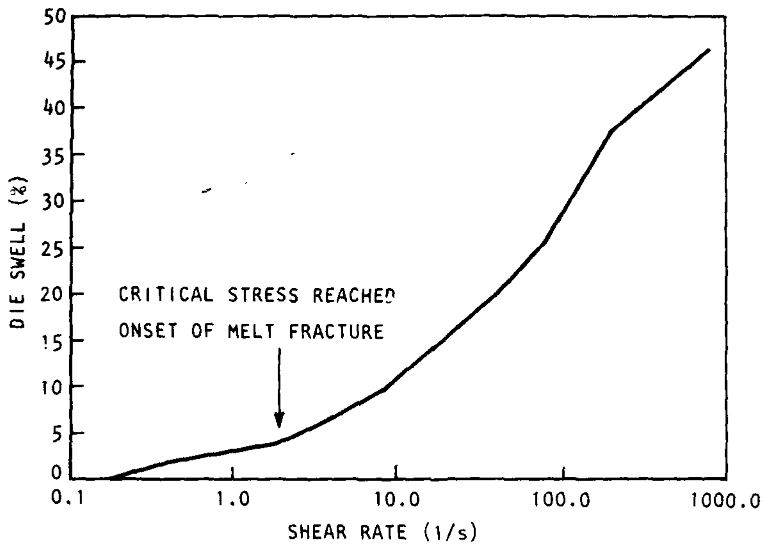

Figure 11. Die swell of well gelatinized unfilled dough GP808 from 3.27 mm diameter die (temperature 50°C)

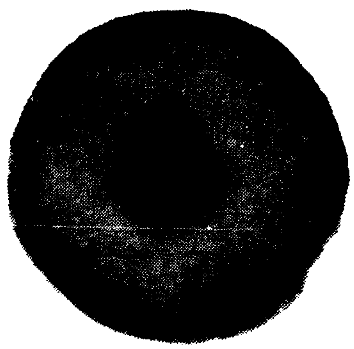

Figure 12. End surface of a single perforate grain of GP801 showing dark bands near the grain surfaces (the perforation is very small)

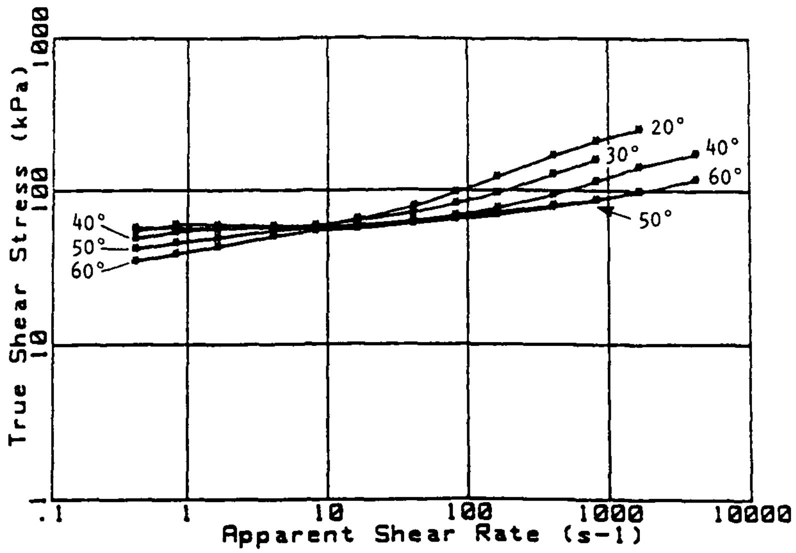

Figure 13. Effect of common mixing and extrusion temperatures on the flow curves of single base doughs

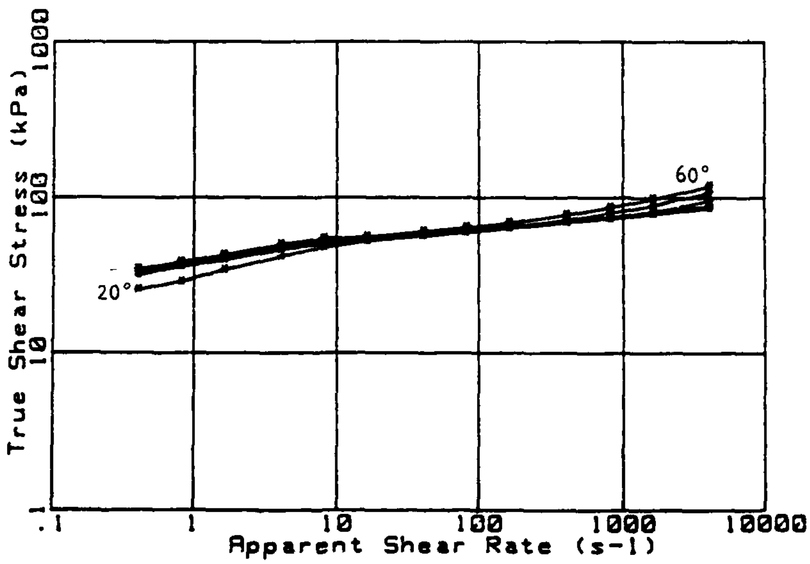

Figure 14. Effect of mixing temperature on the flow curves of single base doughs measured at an extrusion temperature of 60°C

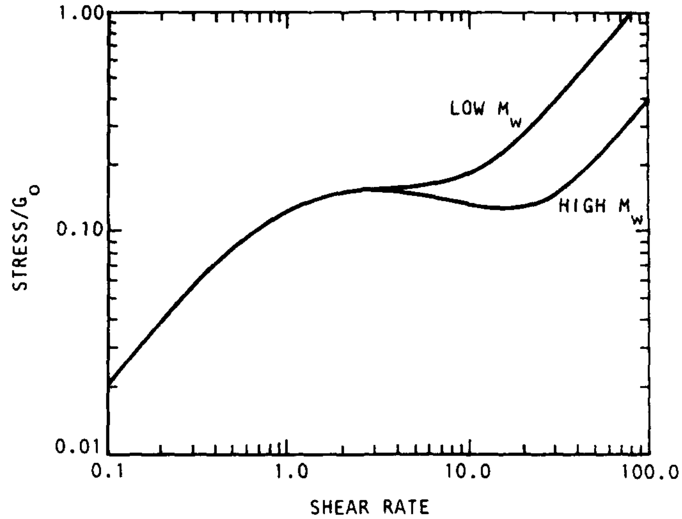

Figure 15. Calculated schematic flow curve of a highly entangled polymer

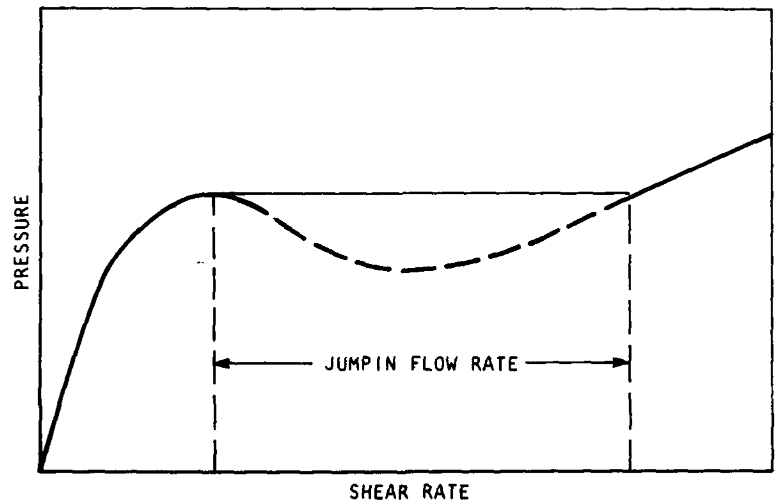

Figure 16. Schematic representation of a flow curve showing a jump in flow rate in pressure controlled flow

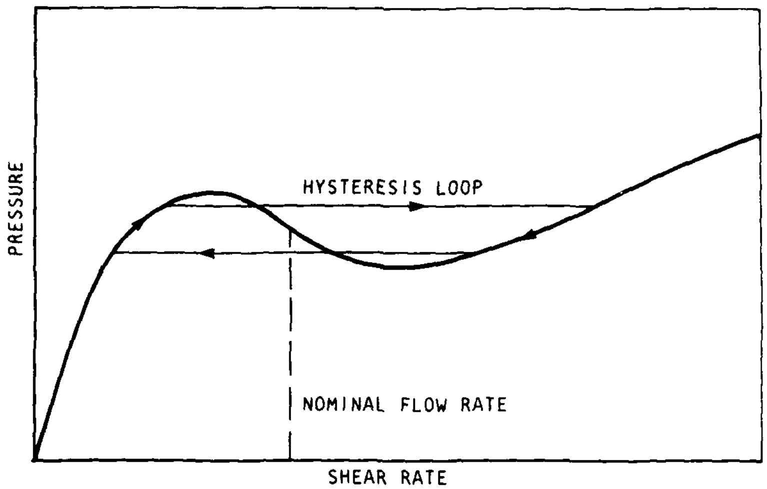

Figure 17. Schematic representation of a flow curve showing possible flow regimes at a nominal shear rate in the negative slope region

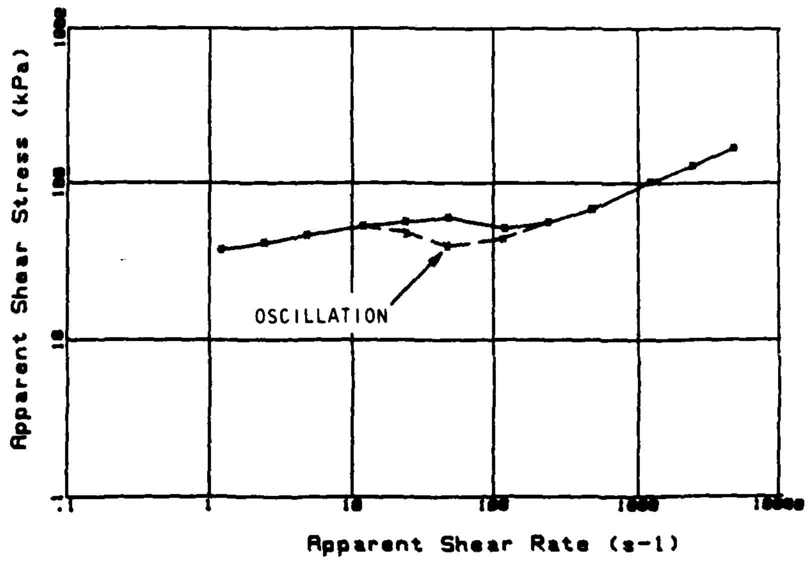

Figure 18. Stress oscillation in the negative slope region of an NQ triple base dough, from reference 1

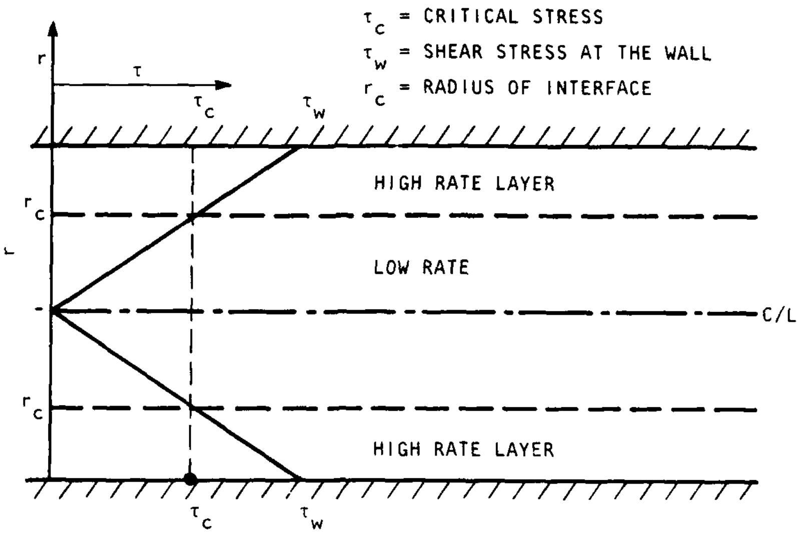

Figure 19. The radial variation of stress and layer formation in flow in a long pipe

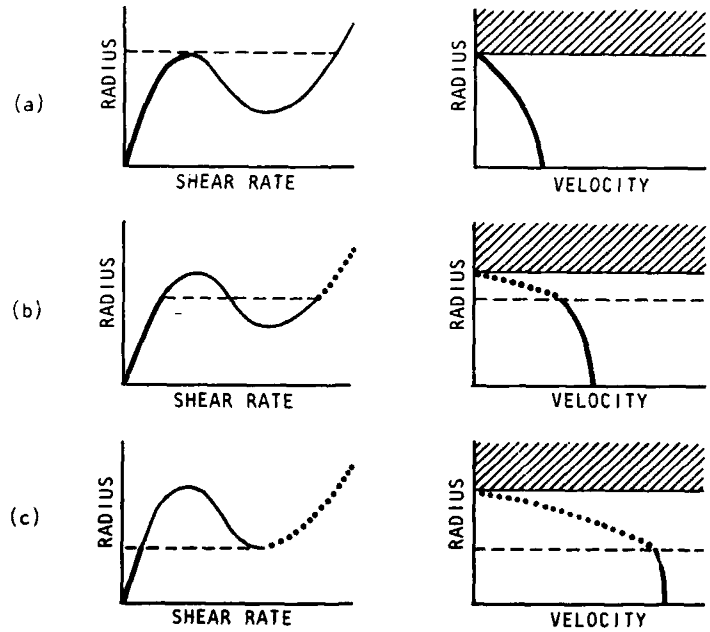

Figure 20. Flow curves and corresponding velocity profiles for various possible layer thicknesses. The high rate regime is dotted

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17 SUMMARY OR ABSTRACT
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Flow curves of triple, double, and single base propellant doughs were determined with an extrusion rheometer. In most cases the curves displayed an inflection which was associated with a critical stress in the dough. The critical stress caused the flow to separate into a high stress layer near the boundary of the flow, and a low stress region in the centre of the flow. The critical stress was also associated with flow instabilities. An explanation of the flow behaviour based on the Doi-Edwards theory is presented.

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